

**AD-A238 260**



**DTIC**

JUL 10 1991

**ANNUAL TECHNICAL REPORT**

to

**AIR FORCE OFFICE OF SCIENTIFIC RESEARCH**

**BOLLING AIR FORCE BASE  
WASHINGTON, D.C. 20332**

on

**ATOMIC APPROACHES TO DEFECT THERMOCHEMISTRY**

**(AFOSR-89-0309)**

**For Period**

**1 April 1990 to 31 March 1991**

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SEARCHED	INDEXED
SERIALIZED	FILED
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**91-04436**



## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		unlimited	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Oregon State University Dept. of Electrical & Computer Engrng.	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Same as 8a	
6c. ADDRESS (City, State and ZIP Code) Corvallis, OR 97331		7b. ADDRESS (City, State and ZIP Code) Same as 8c	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR	8b. OFFICE SYMBOL (if applicable) NE	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-89-0319	
8c. ADDRESS (City, State and ZIP Code) Bolling Air Force Base, Washington, D.C. 20332		10. SOURCE OF FUNDING NOS.	
11. TITLE (include Security Classification) ATOMIC APPROACHES TO DEFECT THERMOCHEMISTRY		PROGRAM ELEMENT NO. 11102F	PROJECT NO. 2306
		TASK NO. B1	WORK UNIT NO.
12. PERSONAL AUTHOR(S) Professor James A. Van Vechten and Associate Professor John F. Wager			
13a. TYPE OF REPORT Annual	13b. TIME COVERED FROM 1/4/90 TO 31/3/91	14. DATE OF REPORT (Yr., Mo., Day) 1991 April 15	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB. GR.	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>The goal of the research program described herein was to apply atomistic thermodynamic theory, Monte Carlo simulation, and experimental analysis to elucidate the identity of point defects in semiconductors as well as to understand their static and dynamic properties. Significant progress has been made in the following nine areas: 1) Direct simulation of atomic diffusion including the effects of realistic boundary conditions, carrier injection and mis-fit strain, 2) Independent measurement of vacancy concentration and diffusivity, 3) Effects of temperature and strain on band offsets and atomic diffusion, 4) Elimination of DX centers from AlGaAs by optically stimulated dislocation climb, 5) Proper analysis of the capacitance-transient due to multiple carrier emission from a highly compensating deep level, 6) C-V analysis and SPICE modeling of ACTFEL devices, 7) DX in AlGaAs, 8) Statistical thermodynamics of ballistic hopping, and 9) Energetics of self-diffusion in GaAs.</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> OTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL J. Van Vechten	22b. TELEPHONE NUMBER (include Area Code) 202 767 4031	22c. OFFICE SYMBOL NE	

# ATOMIC APPROACHES TO DEFECT THERMOCHEMISTRY

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## GOAL

To apply atomistic thermodynamic theory, Monte Carlo simulation, and experimental analysis to elucidate the identity of point defects in semiconductors as well as to understand their static and dynamic properties.

## TECHNICAL ACCOMPLISHMENTS

1. Direct Simulation of Atomic Diffusion including the Effects of Carrier Injection and Junction Mis-Fit Strain: "Resolving Defect Mega-Controversy by Giga Event Monte Carlo Simulation of the Macro-Consequences of Atom-Level Assumptions on Microcomputers at Nano-Cost," J.A. Van Vechten, U. Schmid, and N.C. Myers in *Defect Control in Semiconductors*, ed. by K. Sumino (North Holland, Amsterdam 1990) p. 41; "VIDSIM - A Monte Carlo Program for the Simulation of Atomic Diffusion in Diamond and Zinc-Blende Structures," U. Schmid, N.C. Myers, and J.A. Van Vechten, *Comp. Phys. Comm.* 58, 329 (1990); "Failure of the "Kick-Out" Model for the Diffusion of Au into Si When Tested by Monte Carlo Simulation," U. Schmid, J.A. Van Vechten, N.C. Myers, and U. Koch, *Mat. Res. Symp. Proc.* 163, 609 (1990); "Atomic Diffusion with Strain and Injection," J.A. Van Vechten, *Mat. Res. Soc. Symp. Proc.* 184, 165 (1990); "Surface Treatment Effects on Atomic Diffusion in Si Explained Without Self Interstitials," J.A. Van Vechten, U. Schmid, and Zhang Q.-S., *J. Electron. Mater.* 20, 431 (1991).

A major and long term goal of this effort is to establish a rigorous understanding of the relationship between atom scale material properties (such as the strengths of bonds between various types of atoms,

vacancy and interstitial formation and migrations energies) and device scale properties that determine the performance, reliability, and yield of electronic devices as well as the parameters required for their production. There is a richly developed body of experimental techniques and a plethora of theoretical approaches to deal with the atom scale class of properties in semiconductors and other electronic materials, but only a very tenuous bridge from them to the device scale problems. Device scale problems are inherently complex. Because of this complexity and of the frantic pressures of economic competition, device development has tended to fail to make use of the atom scale information and instead to rely on cut-and-try approaches.

The cut-and-try atmosphere of device development has spawned a number of semi-empirical models for the critical diffusion and interaction processes which are parameterized to fit the data base at hand. They assert formulae with no rigorous derivation and assign atom level parameters with no regard to the results of atom level experiments. Most of these fail badly when extrapolated to the lower temperatures, smaller dimensions, non-one-dimensional diffusions, and much sharper gradients characteristic of advancing technology. They also tend to contradict one another and promote unproductive bickering.

We noticed that the advance of computing technology, particularly of microcomputer power and availability, make it now practical to do direct simulations of atom scale processes on the scale of modern devices. As several billion calculations are required for each interesting case, such a project was heretofore regarded as impossibly tedious. We have developed, demonstrated, and published the VIDSIM program which bridges the gap between the atom level and the device level on microcomputers at very low incremental cost and in reasonable time. Unlike almost all other Monte Carlo simulations, VIDSIM does not invoke any differential equations. It simply works out the macroscopic consequences of whatever set of atom level assumptions and parameters the user wishes to use. We submit that most of the bickering, failure of extrapolations, and wasted effort in the field should be eliminated when all concerned can see for themselves what does and what does not rigorously follow from the atom level to the device level or vice versa.

Our first major success in this effort has been the elimination of all credibility from the so called "kick-out" mechanism for atomic diffusion in Si. This model assumes that host interstitials mediate the major

part of host and dopant diffusion by exchanging places with host or impurity atoms on substitutional sites. Advocates usually assume that vacancies are not able to annihilate these host interstitials. We have shown that, contrary to wide spread belief based on faulty analysis of differential equations, the "kick out" mechanism of diffusion, can not produce a two sided, "U shaped", profile from a one sided in-diffusion of Au or other transition metals that diffuse primarily as impurity interstitials but occupy predominately substitutional sites. We have identified the error in the previous analysis (of others) which led to the false conclusion. We have devised a computer "bug", which when introduced to the simulation can force the inconsistent assumptions of the previous analysis to occur (in a plainly unphysical manner) which will then produce the result claimed by these proponents where the unphysical condition holds. As two sided profiles are firmly established in certain cases, this result eliminates a major class of models that have been advocated to explain them.

We have shown that the fact that one sided in-diffusion of Au does produce a two sided profile of substitutional Au does prove that Si self interstitials can play no significant role in thermal processes in Si. Furthermore, several surface treatment effects which others have claimed require Si self interstitials can be naturally explained without them. (See J. Electron. Mat. 20, 431 (1991), which is in a special issue devoted to diffusion and which was edited by A.F.W. Willoughby, an acknowledged expert on the subject.)

The kick-out mechanism has also been invoked for diffusion in GaAs and other III-V semiconductors. We are working to resolve that issue now.

We have shown that a simple version of the Frank Turnbull mechanism for atomic diffusion does produce a two side profile of substitutional impurities from a one sided source, as is often observed. Moreover, the detailed shape of the profile depends on surface boundary conditions in a degree and manner not previously appreciated in the field. By adjusting assumptions in a plausible way, the simple model can be made to fit experimental data.

We have made what seem to be first ever observations of the distinctions between the result of in-diffusion from an absorbing boundary condition, which seems to be the physically realistic case for an interface to a second phase (e.g., vacuum or a melt or a eutectic), and the coherent boundary to a surface

of constant concentration. The latter was the case considered by Einstein in his study of Brownian motion. Well known results of Einstein's study, e.g., the error function complement relation, do not occur for the absorbing boundary condition, but the distinctions are subtle if one does not know a priori the magnitude of the diffusivity of the diffusing species.

2. Independent Measurement of Vacancy Concentration and Diffusivity by Precise Time-Dependent Measurement of Thermal Expansion at Constant Temperature: R.K. Graupner, T.K. Monson and J.A. Van Vechten, TBP.

Advances in interferometry over the past decade have made it practical to measure variations in the dimension of a macroscopic sample with a precision better than one Angstrom mean surface displacement over periods of many hours. Thus, one can now measure the expansion or contraction of a single crystal sample held at constant temperature as vacancies (and interstitials if significant) diffuse in or out of the bulk to equilibrate the concentrations of these point defects with their source/sink, which is the sample surface. By measuring the absolute value of this expansion at a particular time, one can deduce the total number of vacancies (minus interstitials) present in the sample at that time. By measuring this as a function of time, one can extract the diffusivity of these native point defects independent of their concentrations. (This is regarded as a major coup in the field because previous measurements give only the product of concentration times diffusivity and some ambiguity as to whether vacancies or self interstitials are dominant.) By doing these measurements at different temperatures, one can detect the presence of multiple components (e.g., interstitials as well as vacancies).

Because the concentration of vacancies expected in Si and other tetrahedral semiconductors is in the 10 parts per million range or lower at manageable temperatures, there would at first seem to be a major problem maintaining T so constant that thermal variation of the lattice constant as T drifts does not mask the effect one is seeking. A crude estimate implies that for 1 cm sized samples, one would have to hold T constant to 0.01 C at 1000 C for 20 hours. This would be quite challenging. We have devised a way

around this problem which offers also an opportunity to advance the art of non-invasive semiconductor temperature metrology. We cut multiple samples each in their equilibrium shape and the same size from one single crystal ingot of the material. We have devised a two zone furnace with vacuum transfer mechanism. We will place one of the sample in each of zones and leave them there long enough to equilibrate at their respective temperatures. We then transfer the sample under test repeatedly between the two zones. We measure the variation in the dimension of the sample under test with respect to the equilibrated sample in its zone. In this way any drift in T, or net evaporation, etc., affects both samples similarly and we measure only the effect of the equilibration of the sample under test.

In doing this, we will have the option of applying feed-back to the furnace heating system so that the dimension of the equilibrated sample is held constant to very high accuracy. This will allow us to prepare samples that are at constant and uniform temperature with a accuracy of perhaps 0.001 C at temperatures relevant to semiconductor processing. We will also have good optical access to the samples. This will afford the opportunity to perfect thermorefectance and other methods of non-invasive temperature measurement. Details of this proposal will be submitted separately.

3. Effects of Temperature and Strain on Band Offsets: "The Temperature Dependence of Band Offsets for Semiconductor Heterojunctions in General and for the Particular Cases of AlAs-GaAs and HgTe-CdTe," J.A. Van Vechten and K.J. Malloy (U. of Cal., Berkeley), J. Phys.: Condens. Matter. 2, 281 (1990); "Thermal Expansion Contributions to Band Gap and Band Offset Temperature Dependences," K.J. Malloy (U. of NM) and J.A. Van Vechten, J. Vac. Sci. Technol. (accepted) TBP (1991).

We have devised a simple theory for the temperature and strain dependences of the valence and conduction band offsets in semiconductor heterojunctions using the thermodynamic point of view. We find this to be a major advance over quantum mechanical approaches to the same problem. We have offered a resolution to conflicts between experimental determinations of band offsets in technically important

heterojunctions by reputable groups using different techniques at different temperatures. We showed that both groups can be right for the conditions they applied. We have also developed the machinery to deal with the consequences of misfit strain and dislocation nucleation on the electronic properties of heterojunctions and upon the point defect diffusion near them.

4. Elimination of DX centers from AlGaAs by Optically Stimulated Dislocation Climb: "Liquidation: the Final Solution for the DX Problem" J.A. Van Vechten, S.-B. Kim, and Zhang Q.-S. and R. Matson (SERI) submitted to the 16th International Conference on Defects in Semiconductors, Lehigh, PA 7/91, TBP.

We studied the effect of dislocation climb on the DX center concentration, [DX], in n-type AlGaAs. We found a definite decrease in [DX] and increase in free electron concentration,  $n$ , concomitant with the climb, which was optically stimulated. Clearly, the DX centers were gettered as lattice sites were added to the dislocation structure and it grew dendritic kinks and the donor dopant atoms (Te) were left behind with less compensation. We hope to be able to develop this into a practical method of removing the DX problem from AlGaAs and other wide bandgap compound semiconductors.

The samples used in this study, which also had partial support from the NSF, were 30% Al and grown by MOCVD by V. Sundraman of Boeing on a standard  $\langle 100 \rangle$  GaAs substrate. Misfit dislocations were nucleated by scratching the surface and then caused to glide in a  $\langle 011 \rangle$  direction by Kr<sup>+</sup> laser scanning irradiation as described by Monemar, Van Vechten et al. (Phys. Rev. Lett. 11, 260 (1978)). This optically stimulated glide process has a sharp power threshold so the dislocations were stopped at boundary formed by an Al mask. The threading parts of the dislocation networks run from the junction up 3 microns to the sample surface near the mask boundary. We caused these threading dislocations to climb by illuminating the sample with a laser or with white light at intensities below the glide threshold, as also described previously. We determined [DX] both by DLTS and by capacitance transient spectroscopy at constant temperature,  $C(t)$ , and determined  $n$  by C-V profiling. In order to have adequate junction area for



these electrical measurements, we made the mask holes 0.2 mm x 0.2mm, which is far larger than the 2 micron size envisioned for practical gettering of discrete devices. Consequently, the gettering process took about 10 hours, a factor of 10,000 more than for the practical masks. The degree of getting was only about 50% for these large mask samples but it is clear that our initial attempts are far from optimum. We hope to have much more complete gettering with the smaller masks and with improved processing.

Lang et al. (Phys. Rev. Lett. 42 1353 (1979) had previously reported that the climb of a threading dislocation in AlGaAs reduced [DX], but this report seems to have been generally forgotten in recent years. Ours seems to be the first attempt to combine these two reports from 1978-1979 to affect defect engineering by optically induced dislocation glide and climb. Part of the reason that Lang et al.'s report has fallen from notice is that many workers in the field have believed models for the DX center, such as that of Chadi and Chang, which hold that the deep center and the donor atom are one and the same. If this "No X" hypothesis were true, it would not be possible to getter the deep center without reducing the net donor doping,  $n$ , also. We submit that this present result, along with several others, completely disprove all "No X" theories for the DX center in AlGaAs.

5. Proper Analysis of the Capacitance Transient due to Multiple Carrier Emission from a Highly Compensating Deep Level, e.g., DX: "Capacitance Transient Due to Multiple Majority Carrier Emission from DX Centers in AlGaAs," S.-B. Kim, J.A. Van Vechten, and Zhang Q.-S., TBP.

Because of the controversial nature of our result for the effect of dislocation climb upon DX center concentration, [DX], just described above, we made a careful study of the capacitance transient at constant temperature,  $C(t)$ , technique which we used to determine [DX]. Almost everyone who uses this technique applies an analysis which assumes (see e.g., D. K. Schroder "Semiconductor material and device characterization" J. Wiley, New York, 1990, Chapt. 7, especially pp. 306) that the deep levels trap and emit free carriers in one transition only, that the applied voltage in the reversed biased condition,  $V_A$ , is much larger than the built in voltage,  $V_{bi}$ , of the junction employed, and that the density of deep centers is much

less than the net doping level. It is now firmly established that the DX center traps at least 2 and more likely 3 electrons (Van Vechten, J. Phys. Cond. Matter. 1, 5171 (1989); Gibart et al., Phys. Rev. Lett. 65, 1144 (1990)). Our  $C(t)$  experiments and those of many other groups are done with  $-V_A \sim V_{bi}$ . The DX centers compensate typically 2/3 or more of the donor doping, which is why there is so much interest in the DX center. Thus, all three of these assumptions made in the standard analysis are invalid for the typical experiment to determine  $[DX]$  in AlGaAs.

We revised the analysis of  $C(t)$  to take account of the facts that the compensation ratio can be large,  $-V_A$  can be about the same as  $V_{bi}$ , and that multiple carriers can be trapped and emitted in several different transitions. We treated the depletion layer,  $W$ , in two sections. The first,  $W_{FP}$ , is that which is depleted by  $V_{bi}$  alone when  $V_A = 0$ , as during the "filling pulse". In  $W_{FP}$  we assume that the compensation ratio, i.e., 1 minus the ratio of the ionized dopant concentration to the net charge density, is invariant in time and, for a homogeneous sample, constant in space. We call this compensation ratio  $g$ . When the junction is reverse biased, the depletion width is wider and the region beyond  $W_{FP}$  contains the majority carriers that have been trapped by the deep centers. In our case these are the electrons that have been trapped by the DX centers. Thus, the compensation ratio in this expanded part of the depletion layer is generally larger than that in  $W_{FP}$  and varies in time as the trapped carriers (electrons) are emitted. We call this compensation ratio  $f(t)$  and take it to be uniform across the expanded part at any given time. With increasing time under reverse bias,  $f(t)$  approaches  $g$ . As this happens,  $W$ , which we determine by double integrating the Poisson integral of these two charge layers, decreases and the junction capacitance,  $C_J(t)$ , increases. It is  $C_J(t)$  that is actually measured.

We have derived generally expressions for  $C_J(t)$  for this two layer model of the depletion region for the cases that a) 2 electrons are emitted in one "negative-U" transition (as per the Chadl Chang model); b) 2 electrons are emitted in two correlated transitions; c) 3 electrons are emitted three correlated transitions (as per the Lang-Logan-Jaros, Van Vechten model) d) 3 electrons are emitted in two transitions, one of which is negative-U; and e) 3 electrons are emitted in three independent transitions. These expressions are somewhat complicated by the standards of the era before the widespread availability of micro computers,

which is probably why this analysis was not done previously. However, we have developed and are distributing a robust fitting program that analyses raw data in terms of any of these assumptions one chooses to use. This program runs on a standard PC (with math coprocessor) in a few seconds.

When applied to our own  $C(t)$  data for the samples described above, we find that for one fixed temperature (e.g., 131 K) all five of the above assumptions can be parameterized to fit the data well enough to pass a 95% statistical confidence test. However, by Arrhenius analysis of the computer fitted parameters through the temperature range 125 to 137 K, we can make a strong argument that options d and e should be discarded for the DX center. Furthermore, the conclusion that [DX] has been reduced by the dislocation climb, and how much this reduction is for a given sample, is quite insensitive to which of the five choices one makes. Thus, we are confident in the validity of the conclusion of the previous section that optically stimulated dislocation climb does reduce [DX] while simultaneously increasing  $n$ .

6. C-V Analysis and SPICE Modeling of ACTFEL Devices: "Capacitance-Voltage Characteristics of Alternating-Current Thin-Film Electron Luminescent Devices," R.C. McArthur, J.D. Davidson, J.F. Wager, I. Khormaei, and C.N. King, Appl. Phys. Lett. 56, 1099 (1990), "Characterization of ZnS:Mn AC Thin-Film Electroluminescent Devices by Capacitance-Voltage Analysis," R.C. McArthur, J.D. Davidson, I. Khormaei, J.F. Wager, and C.N. King, Acta Poly Technica Scandinavia Ph 170, 181 (1990); "Aging Instabilities of ZnS:Mn AC Thin-Film Electroluminescent Devices," J.D. Davidson, J.F. Wager, I. Khormaei, and C.N. King, Acta Polytechnica Scandinavia Ph 170, 185 (1990); "Electrical Characterization and Modeling of Alternating-Current Thin-Film Electroluminescent Devices," J.D. Davidson, J.F. Wager, I. Khormaei, C.N. King, and D. Williams, IEEE Trans. Electron Devices (submitted).

The standard method for characterizing the electrical properties of alternating-current thin-film electroluminescent (ACTFEL) display devices is  $h\nu$  charge-voltage (Q-V) analysis. We have developed a complementary technique, the capacitance-voltage (C-V) technique for ACTFEL characterization. Since

ACTFEL device operation depends upon the application of a large amplitude (300-450 V peak-to-peak) AC waveform, conventional small-signal C-V analysis is precluded. Instead, we perform our C-V analysis by sampling the instantaneous voltage across a current-limiting resistor placed in series with the ACTFEL device and processing these sampled signals digitally to obtain the C-V curve. Q-V, Q-t, and I-t analysis can be performed in the same manner.

Our motivation for developing this technique is to study the properties of point defects in the II-VI semiconductor ZnS, as manifest by the electrical properties of commercial devices. Specially fabricated, commercial quality devices are fabricated by Planar Systems, Inc., Beaverton, Oregon, for this purpose.

The slope of the C-V curve in the transition region is shown to be related to the density of interface states at the ZnS-insulator interface. Commercial devices manufactured by Planar Systems are found to have moderate interface state densities which are independent of the operation time of the display. In contrast, commercial devices supplied by Finlux, Helsinki, Finland, initially have a low density but the interface state density increases dramatically as the devices are operated. We are currently trying to understand the physical nature of these interface defects and their dynamics with operation time.

We have also recently applied SPICE modeling in conjunction with a simple equivalent circuit for the ACTFEL device in order to assist in the interpretation of C-V curves. We have found SPICE modeling to be invaluable as a tool for clarifying ACTFEL device physics issues.

The C-V technique has proven to be useful for experimentally investigating the aging instabilities inherent in present art ACTFEL devices. We are performing variable-temperature aging studies on ZnS:Mn ACTFEL devices in an attempt to deduce the microscopic mechanism responsible for aging instabilities. Preliminary analysis of the kinetic data suggests that two aging mechanisms are operational. One mechanism, which dominates at low-temperatures and has a small activation energy, we attribute to electron injection and trapping at the ZnS/insulator interface. The second mechanism is important at and above room temperature and is characterized by a larger activation energy; we attribute this aging mechanism to atomic migration or interdiffusion which is driven by hot electron recombination.

We are applying atomistic thermodynamic modeling to these problems in order to attempt to understand on a microscopic scale the nature of these device properties.

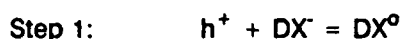
7. DX in AlGaAs: "Transient Decay of Persistent Photoconductivity in  $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ ," T.W. Dobson, L.V.A. Scalvi, and J.F. Wager, J. Appl. Phys. 68, 601(1990).

One of the peculiarities of the DX center in AlGaAs is the fact that it exhibits persistent photoconductivity (PPC) at low temperatures ( $\leq 50\text{K}$ ). At intermediate temperatures (80-100K) the PPC is not entirely persistent and exhibits a decay with time. We have measured this transient decay of PPC (TDPPC) as a means of exploring the donor- or acceptor-like nature of the DX center. We analyze our experimental data by performing a computer simulation which involves the nonequilibrium capture kinetics of electrons from the conduction band into the DX center and a concomitant change in mobility due to ionized impurity scattering. We then simulate six models for the DX center. We find excellent quantitative agreement between experiment and the simulation for the DX model of Chadi and Chang [Phys. Rev. B39, 10063 (1989)], which assumes DX to be a negative-U acceptor with intrinsic self-compensation, plus a photo-induced shallow donor.

8. DX in AlGaAs: S.B. Kim and J.F. Wager, J. Appl. Phys. (in preparation).

The low-temperature minority carrier capture cross section for the DX center has been measured for the first time. The minority carrier capture (MCC) experiment is accomplished by photo-injection of holes into the space charge region of a semitransparent Schottky barrier on AlGaAs. We find the capture cross section to be of magnitude  $2 \times 10^{-19} \text{ cm}^2$  and independent of temperature over the range 30-70K. According to the theory of Ridley [Solid State Electronics 21, 1319 (1978), J. Phys. C. 14, 1255 (1981)] and the experimental work of Henry and Lang [Phys. Rev. B15, 989 (1977)], a low-temperature capture cross section of this magnitude and which is temperature-independent is indicative of hole capture by a coulombically neutral trap. Thus, we conclude that hole capture occurs into a neutral DX trap state. We note that this

result can be reconciled with the DX model of Chadi and Chang [Phys. Rev. B39, 10063 (1989)] if the capture is postulated to occur by the following two-step process in which the second step is rate-limiting:



9. Statistical Thermodynamics of Ballistic Hopping: "A Statistical Thermodynamic Derivation of the Ballistic Model for Vacancy Migration," J.F. Wager, Phil. Mag. A (1991), in press.

Much of our work on defect dynamics is based on the validity of the Ballistic Model (BM) [J.A. Van Vechten, Phys. Rev. 12, 1247 (1975)] which asserts (essentially) that the enthalpy for vacancy migration is determined by the kinetic energy of the atom which hops into the vacancy. We have previously extended the BM hypothesis to calculate the entropy of migration for nearest-neighbor hopping [T.W. Dobson, J.F. Wager, and J.A. Van Vechten, Phys. Rev. B12, 2962 (1989)].

The primary impetus for this work is that the migration entropy is estimated by our previous method [Dobson et al.] is anomalously large when compared to known trends for self-diffusion in elemental metals. The statistical thermodynamic derivation leads to a migration enthalpy and entropy qualitatively similar, but not identical, to that given previously. The statistical thermodynamic correction to the migration enthalpy is of negligible importance. In contrast, the correction to the entropy of migration which arises from the statistical thermodynamic derivation is found to be significant and must be employed in order to obtain agreement with experimental values for elemental metals.

10. Energetics of Self-Diffusion in GaAs: "Energetics of Self-Diffusion in GaAs," J.F. Wager, J. Appl. Phys. 69, 3022 (1991).

In order to provide insight into the nature of the mechanism of self-diffusion in GaAs, two kinds of atomistic thermodynamic calculations are performed. First, the activation enthalpy of the saddle point

configuration for various modes of vacancy-mediated self-diffusion is estimated. The primary conclusion of the analysis is that if vacancies are available in equilibrium concentrations vacancy migration by second nearest-neighbor hopping (2nnh) is found to be the energetically most favorable mechanism of self-diffusion, independent of the Fermi-level position. The second type of atomistic thermodynamic calculation performed is estimation of the activation entropy for various modes of vacancy migration. The primary conclusion of the analysis is that vacancy migration by 2nnh is consistent with activation entropies of order  $6 k_B$  whereas vacancy migration by nearest-neighbor hopping (nnh) is characterized by much larger activation entropies of order  $20 k_B$ .

Our activation enthalpy and entropy analysis leads to the conclusion that experimental self-diffusion and interdiffusion data with abnormally large diffusivity prefactors and activation energies [as summarized, for example, by T.Y. Tan and U. Gösele, Appl. Phys. Lett 52, 1240 (1988)] cannot be explained in terms of any vacancy mediated self-diffusion mechanism in which vacancies are present in equilibrium concentrations. Rather, we propose that Ga self-diffusion or interdiffusion processes which are characterized by large prefactors ( $\sim 10^7$ - $10^8 \text{ cm}^2 \text{ s}^{-1}$ ) and activation energies ( $\sim 6 \text{ eV}$ ) involve cation Frenkel pair formation. This mode of self-diffusion is expected to be dominant when surface vacancy generation is precluded and vacancies can only be generated in the bulk of the semiconductor by the creation of an interstitial-vacancy pair.

The results of our activity are discussed in detail in the attached reprints and preprints.